Introducció als sistemes polielectrònics. Mètodes Variacional i Pertorbacional.

1. L'àtom d'heli i el forat de Coulomb

$$\mathcal{H} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = h(1) + h(2) + V(1,2)$$

Com $V = \frac{1}{r_{12}}$ si $r_{12} \to 0$ $V \to \infty$ $\rightarrow$ $\psi(r_1 = r_2) \to 0$

Forat de coulomb

CORRELACIÓ

$\Rightarrow$ $\boxed{\psi(1,2) \neq \phi(1)\,\phi'(2)}$ $\Rightarrow$ impossible ressolució analítica.

2. Model de partícules independents

Rebutgem $V(1,2)$ $\Rightarrow$ $\Psi \approx \phi(1)\,\phi'(2)$; ϕ hidrogenoide

- àtom heli $E = 2\,\varepsilon_0$; $\varepsilon_0 = -\frac{Z^2}{2}\frac{1}{n^2}$ a.u. $\begin{cases} E_{teor} = -4 \text{ a.u.} \\ E_{exp} = -2.9 \text{ a.u.} \end{cases}$

$\rightarrow$ apantallament (suposem $Z^* = Z - S$)

CÀLCUL $E = 2.9 = -\frac{(Z-S)^2}{2}$ $\rightarrow$ $S = 0.3$ $\rightarrow \begin{cases} PI = -\varepsilon^0 = 1.45 \\ PI_{exp} = 0.9 \text{ a.u} \end{cases}$

$\Rightarrow$ $1s < 2s = 2p < 3s = 3p = 3d \ldots$

---> CAL CONSIDERAR LA CORRELACIÓ QUE DERIVA DE $V(1,2)$

3. El terme de repulsió

Assumim $\Psi = \prod_i \phi_i(r_i)$ però calculem E com $\langle \Psi | \mathcal{H}_{EXACTE} | \Psi \rangle$

$\rightarrow$ Àtom heli $E = -2.75$ a.u.

Configuracions electròniques s sp sp sdp sdp sfdp...

e.g. Ni $4s^2\,3d^8$ malgrat que $\varepsilon(4s) > \varepsilon(3d)$

OK sistema periòdic

$\Rightarrow$ Pregunta perquè $\langle \Psi^0 | \mathcal{H}_{EXACTE} | \Psi_0 \rangle$?

$\Rightarrow$ RESPOSTA : MÈTODE VARIACIONAL ó PERTORBACIONAL

4. Mètode Variacional

Teorema: Si Ψ_0 compleix les condicions de contorn,

$$E_{aprox} = \frac{\langle \Psi_0 | \hat{\mathcal{H}} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \geq E_0$$

Demostració: $\Psi_0 = \sum c_i \chi_i$ on $\hat{\mathcal{H}} \chi_i = E_i \chi_i$

$$E_{aprox} = \frac{\sum c_i c_j \langle \chi_i \hat{H} \chi_j \rangle}{\sum c_i c_j \langle \chi_i \chi_j \rangle} = \frac{\sum c_i^2 E_i}{\sum_i c_i^2} \geq \frac{\sum c_i^2 E_0}{\sum c_i^2} = E_0.$$

4.1 Mètode de les variacions lineals

Cas particular on $\Psi_0 = \sum_i c_i \chi_i$ on χ_i és un conjunt de funcions arbitràriament triat.

$$E_{aprox}(c_1 c_2 \cdots c_n) = \frac{\sum_{ij} c_i c_j \langle \chi_i \hat{\mathcal{H}} \chi_j \rangle}{\sum_{ij} c_i c_j \langle \chi_i \chi_j \rangle} = \frac{\sum_{ij} c_i c_j h_{ij}}{\sum_{ij} c_i c_j s_{ij}}$$

La millor E_{aprox} la mínima : $\partial E_{ap} / \partial c_i = 0$

$$\frac{\sum c_j h_{ij}\, DEN - \sum c_j s_{ij}\, \underbrace{NUM}_{E_{ap}\, DEN}}{DEN^2} = 0$$

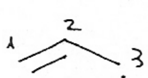
$$\longrightarrow \sum c_j (h_{ij} - E_{ap} s_{ij}) = 0 \longrightarrow \begin{cases} \mathbb{H} \mathbb{C} = E_{ap} \mathbb{S} \mathbb{C} \\ \det | \mathbb{H} - E_{ap} \mathbb{S} | = 0 \end{cases}$$

4.2 Mètode Huckel

: com una aplicació del mètode de les variacions lineals

$\Psi = \sum_i c_i \chi_i$; $\chi_i = 2p_z^c$. s'aproxima $S_{ij} = \delta_{ij}$

$\hat{h}$ desconegut $\longrightarrow$
$\langle \chi_i | h | \chi_i \rangle = \alpha$
$\langle \chi_i | h | \chi_{i\pm1} \rangle = \beta$
altres $= 0$

e.g. 

$$\longrightarrow \begin{bmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{bmatrix} = 0 \quad \text{on} \quad x = \frac{\alpha - E}{\beta}$$

$\Rightarrow$ Aquest mètode justifica $\langle \Psi_0 | \hat{\mathcal{H}} | \Psi_0 \rangle$.

5. Mètode perturbacional

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^0 + \hat{\mathcal{H}}' \; ; \qquad \hat{\mathcal{H}}^0 \chi_i = E_i^0 \chi_i \qquad \langle \hat{\mathcal{H}}^0 \rangle \gg \langle \hat{\mathcal{H}}' \rangle$$

$$\hat{\mathcal{H}}_\lambda = \hat{\mathcal{H}}^0 + \lambda \hat{\mathcal{H}}' \Rightarrow \boxed{\hat{\mathcal{H}}(\lambda) \Psi(\lambda) = E(\lambda) \Psi(\lambda)}$$

$$(\mathcal{H}_0 + \lambda \mathcal{H}')(\Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 \dots) = (E_0 + \lambda E_1 + \lambda^2 E_2 + \dots)(\Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \dots)$$

λ^0 : $\mathcal{H}_0 \Psi_0 = E_0 \Psi_0 \Rightarrow \boxed{\Psi_0 = \chi_0}$

λ^1 : $(\mathcal{H}_0 - E_0)\Psi_1 = (E_1 - \mathcal{H}')\Psi_0$

λ^2 : - - — — — — - —

$\vdots$

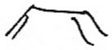
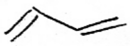
$\langle \Psi_0 | * \Rightarrow 0 = E_1 - \langle \Psi_0 | \mathcal{H}' | \Psi_0 \rangle \Rightarrow E_1 = \langle \Psi_0 | \mathcal{H}' | \Psi_0 \rangle$

$\Rightarrow$ Justifica que calcule $\langle \Psi_0 | (\mathcal{H}_0 + \mathcal{H}') | \Psi_0 \rangle \Leftarrow$

$$|\Psi_1\rangle = \sum_{i \neq 0} c_i \chi_i$$

$\langle \Psi_j | * \quad (\mathcal{H}_0 - E_0) \sum_{i \neq 0} c_i \chi_i = (E_1 - \mathcal{H}')\chi_0$

$$\rightarrow \quad c_j = - \frac{\langle \chi_j | \mathcal{H}' | \chi_0 \rangle}{E_j - E_0} \; ; \quad \Psi_1 = - \sum_{i \neq 0} \frac{\langle \chi_j H' \chi_0 \rangle}{E_j - E_0} \chi_j \; , \dots \text{ etc}$$

Example:  vs 

$$H^0 = \begin{bmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & 0 \\ 0 & 0 & \beta & \alpha \end{bmatrix} \qquad \mathcal{H}' = \begin{bmatrix} 0 & 0 & 0 & \beta' \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \beta' & 0 & 0 & 0 \end{bmatrix}$$

$$E^{(1)} = \langle \Psi_0 | \mathcal{H}' | \Psi_0 \rangle = \sum_{ij} c_i c_j \langle \chi_i | \mathcal{H}' \chi_j \rangle$$

si $\Phi^0 = (a, b, c, d) \rightarrow E^{(1)} = 2ad\beta'$